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RESEARCH MEMORANDUM

PRELIMINARY INVESTIGATION OF CORROSION BY MOLTEN SODIUM HYDROXIDE FLOWING IN TUBES OF AISI 347 STAINLESS STEEL, INCONEL, AND NICKEL HAVING AVERAGE OUTER-WALL TEMPERATURES OF 1500° F AND A CIRCUMFERENTIAL TEMPERATURE GRADIENT OF 20° F

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

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PRELIMINARY INVESTIGATION OF CORROSION BY MOLTEN SODIUM HYDROXIDE FLOWING IN TUBES OF AISI 347 STAINLESS STEEL, INCONEL, AND NICKEL HAVING AVERAGE OUTER-WALL TEMPERATURES OF 1500° F AND A CIRCUMFERENTIAL TEMPERATURE GRADIENT OF 20° F

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SUMMARY

In an earlier report (reference 1) an apparatus suitable for determining corrosive effects of hot flowing liquids on various container materials is described. With this apparatus, experiments were performed using molten sodium hydroxide flowing at 15 feet per second in tubes of AISI 347 stainless steel, Inconel, and type A nickel having average outer-wall temperatures of 1500° F and a circumferential temperature gradient of 20° F. Extensive corrosion and mass transfer to regions of reduced temperature was observed.

INTRODUCTION

Molten sodium hydroxide is advantageous in many ways as a nuclear-reactor coolant and moderator. It has the disadvantage, however, of being extremely corrosive to most common container and structural materials. As far as is known, the few container materials which have been considered promising, such as nickel and silver, have been subjected only to static tests at constant temperature. In a reactor, the sodium hydroxide will be flowing at substantial velocities, and large temperature differences (of the order of several hundred degrees) will exist in the circulating system. Under such conditions, significant quantities of even a relatively insoluble container material may be dissolved from the hotter portions of the system, transported in the flowing liquid to the cooler portions, and there be deposited on the container walls. Inasmuch as any such mass transfer occurring would be expected to be a function of both velocity and temperature difference, it is doubtful whether results of static corrosion tests can be accepted as conclusive. Dynamic tests, although desirable, have previously been limited because of the expensive and complicated setup required. In addition, it was difficult to obtain a system made up of only the test material, and the introduction of other materials into the system added to the difficulty of interpreting the experimental results.

In reference 1, an apparatus is described which permits circulation of a fluid in a closed loop of tubing without the need of pumps, seals, or bearings. This apparatus has been used in preliminary tests with sodium hydroxide flowing in tubes of AISI 347 stainless steel, Inconel, and type A nickel and the results are reported herein. All tests were run at a temperature of 1500° F and a fluid velocity of 15 feet per second. A portion of the tube was cooled by an air blast so that a circumferential temperature differential of approximately 20° F existed.

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It is reemphasized that these results are preliminary and of a qualitative nature.

APPARATUS AND PROCEDURE

Circulating apparatus. - A schematic diagram of the circulating apparatus is shown in figure 1. A horizontal circular plate is attached at its center (by means of a bearing) to the crankpin of a vertical crankshaft. A compound parallelogram-type restraining mechanism attached to the edge of the plate and to the supporting structure maintains the plate in fixed orientation with respect to the mounting structure. Rotation of the crankshaft results in motion of the plate such that any point on its surface describes a circle with radius equal to the crank throw. The crankshaft is driven by a motor with a variable-speed transmission. As the crankshaft is rotated, the point on the toroid which is farthest from the center of rotation is on a straight line passing through the centers of the crankshaft and the crank pin. When the filled volume of the toroid is roughly between 10 and 40 percent of capacity, a slug of fluid is formed, the center of gravity of which will tend to approach the point of greatest radius because of centrifugal force. This point of greatest radius makes one revolution for every revolution of the crankshaft, and hence the fluid within the toroid makes one circuit of the toroid for every revolution of the crankshaft.

Fabrication of specimens. - Specimens of each of the container materials were fabricated in the form of a vented toroid having the dimensions shown in figure 2. After an appropriate cleaning procedure, the toroids were loaded with enough sodium hydroxide pellets (of purity shown in table I) to result in approximately 40-percent filling when molten. For the 347 stainless-steel specimen, closure of the toroid was accomplished by means of a compression fitting. A more satisfactory method, used on subsequent specimens, proved to be welding as shown in figure 2. Closures were tested for leaks by a mass-spectrometer-type leak detector. The toroids were instrumented with thermocouples and wrapped with beaded heater wires. Asbestos insulating tape covered the heater wires with the exception of the uninsulated sector of the toroid shown in figure 2. In order to remove the entrapped air and water vapor from the sodium hydroxide pellets, the toroids were evacuated while gradually being heated to just above the melting point of the caustic. Following this procedure, each specimen was filled with purified helium, the vent tube was crimped shut, and the end sealed with silver solder. The instrumented specimen was then installed in the circulating apparatus as shown in figure 3.

Test procedure. - The mounted specimen was heated until the lowest temperature on the outside surface of the toroid was at least 650° F. A representative temperature distribution around the toroid during this heating period is shown in figure 4(a). The mounting plate speed was then gradually increased from zero to test speed (corresponding to a fluid velocity of 15 ft/sec for all tests reported herein). Electric power to the heaters was increased until the insulated portion of the specimen reached 1500° F, test temperature for these specimens. An automatic controller maintained the specimens at temperature. The flow of air through a nozzle directed at the uninsulated sector of the specimen was then started and resulted in a toroid wall temperature, in this region, about 20° F lower than the rest of the specimen. A typical temperature distribution around the toroid after reaching test conditions is seen in figure 4(b). The uniform temperature level of the tube, excluding the cooled sector, indicated that flow existed within the toroid. Proof of the existence of slug flow was obtained by later examination of the tube bore.

Examination of specimens. - On completion of a run, the duration of which varied from $8\frac{1}{2}$ to 24 hours, the toroid was opened by making one transverse cut through the tubing. The contents were dissolved with distilled water and collected for analysis. When washing a preliminary 347 stainless-steel specimen, it was noted that an odorless combustible gas was given off. On subsequent specimens, the gas was collected for analysis. After the toroid was thoroughly washed, it was sectioned by making additional transverse cuts through the tubing between thermocouples. Visual inspection of all sections was followed by microscopic examination of metallographic specimens from the hot, cooled, and welded sections. A measure of the extent of mass transfer was obtained by determining the ratio of the weight of a specimen from the cooled sector to one of like external dimensions from the hot sector.

RESULTS

Chemical analyses of pertinent specimen components are presented in table II along with the volume of hydrogen evolved upon water solution of the toroid contents. Also given is the weight ratio of specimens taken from the cooled and hot sectors of the toroids and remarks concerning the physical condition of the specimens. In all cases in which the composition of the solution is available, it is seen that certain components of the container material were preferentially attacked.

Macroexamination

Examination of the specimens revealed that a metallic deposit was formed on all cooled surfaces ranging from a thin film in the case of
347 stainless steel (fig. 5) to a layer of relatively large crystals on 2366
the Inconel (fig. 6) and nickel (fig. 7). The appearance of the hot surfaces differed according to the type of attack, those of the stainless steel and Inconel being dull and discolored from corrosion products, whereas that of nickel was bright and seemed free from corrosion products.

Microscopic Examination

AISI 347 stainless steel. - The 347 stainless steel suffered intergranular corrosion in both the hot and cooled areas as shown in figure 8. In the regions shown in figure 8, the depth of the corrosion layer was 0.016 inch after 21 hours of running time (6.7 in./year).

Inconel. - The depth of the corrosion layer on both the hot and cooled sections of the Inconel specimens (fig. 9) was, where measured, 0.004 inch after 24 hours of running time (1.5 in./year). The layer of crystals deposited on the cooled portion of the Inconel was about 0.018 inch thick but varied somewhat about the periphery of the bore. These as well as the foregoing specimens were nickel plated prior to polishing the section to preserve the corrosion layer and unfortunately the plating is not readily distinguishable from the crystalline deposit shown in figure 9(b).

A photomicrograph of a section taken from the welded closure after a 24 hour run is shown in figure 10. The weld was made by conventional heliarc technique.

Type A nickel. - Photomicrographs of specimens taken from the $8\frac{1}{2}$ hour test of A nickel are shown in figure 11. The hot section (fig. 11(a)) revealed a thin corrosion layer (0.00015 in. or 0.15 in./year). No such layer was noted on the cooled section (fig. 11(b)) but metallic crystals had been deposited to a depth of 0.015 inch.

Metallographic examination of the 21-hour nickel test (fig. 12) indicated similar behavior, the corrosion layer on the hot surface (fig. 12(a)) being 0.00025 inch (0.10 in./year) and the crystalline deposit on the cooled surface amounting to 0.012 inch (fig. 12(b)).

Consistently good welds on type A nickel have not been achieved. This has resulted in several unreported runs which were terminated prematurely by weld failure. These failures seem to result from porosity in the welds as shown in figure 13 (weld made by modified heliarc technique). Several techniques have been tried with varying success but as yet no completely reliable method has been found.

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SUMMARY OF RESULTS

A corrosion investigation was conducted with molten sodium hydroxide flowing at a velocity of 15 feet per second, a temperature of 1500° F, and a circumferential temperature gradient of 20° F in tubes of the following container materials: AISI 347 stainless steel, Inconel, and type A nickel. The investigation indicated that:

1. In all cases certain components of the container material were preferentially attacked.

2. Of the three container materials tested, AISI 347 stainless steel was attacked the deepest with intergranular penetration to an apparent depth of 0.016 inch after 21 hours of operation.

3. Relatively heavy deposits of crystals were built up on the cooled sectors (about 20° F below nominal operating temperature). of both the Inconel and type A nickel specimens in operating periods of 24 and 21 hours, respectively.

Lewis Flight Propulsion Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, August 15, 1951.

REFERENCE

1. Desmon, Leland G., and Mosher, Don R.: Preliminary Study of Circulation in an Apparatus Suitable for Determining Corrosive Effects of Hot Flowing Liquids. NACA RM E51D12, 1951.

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TABLE I - ANALYSIS OF SODIUM HYDROXIDE PELLETS

Material	Percent by weight
Assay (NaOH)	97.6
Chloride (Cl)	0.005
Iron (Fe)	.001
Other heavy metals (as Ag)	.000
Carbonate (Na_2CO_3)	.32
Phosphate (PO_4)	.000
Silica and NH_4OH precipitate	.000
Total nitrogen (as NH_3, NO_2)	.001
Sulfate (SO_4)	.000

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TABLE II - SUMMARY OF TESTS[1]

Specimen	Composition			Test duration (hr)	Volume of hydrogen evolved from water solution of tube contents (liters)	Metallic clusters in solution			Composition of solution			Deposit on cooled sector		Weight ratio (cooled sector / hot sector)	Remarks
	Alloy	Constituent	Percent			Constituent	Percent	Weight (grams)	Constituent	Percent	Weight (grams)	Constituent	Percent		
2	AISI 347 stainless steel	Cr Ni C Cb	17-19 9-12 0.08 max 10 × C	21	5.5	Fe Ni Mn Cr	77.2 18.1-19.7 3.8- 4.0 0.70- .75	>1.5	Fe Cr Mn Ni NaOH	54.6 38.9 5.4 .0	1.83 88	Fe Ni Cr O_2	85 17 2 remainder	Air blast too localized to permit significant weight determination	Intergranular attack to a depth of 0.016 inch (6.7 in./year). Metallic film deposited on cooled sector.
4	Inconel	Ni Cr Fe Cu Mn Si C S	75 min 12-15 9 max 0.5 max 1.0 max .5 max .15 max .02 max	24	0.4	None			Solution lost during evaporation			Ni Fe Cr O_2	85.8 5.1 4.0 remainder	1.04	Corrosion layer 0.004 inch deep (1.5 in./year). Crystalline deposit on cooled sector 0.018 inch thick.
7	A nickel (99.4 Ni + Co)	Ni Cu Fe Mn Si C S	99 min 0.25 max .5 max .35 max .5 max .2 max .02 max	$8\frac{1}{2}$	Gas analysis not significant; toroid leaked during run	None			Ni Fe Cu Mn Cr Co NaOH	88.2 3.8 3.2 2.8 1.7 .3	0.185 93.2	Nickel		1.06	Test terminated by weld failure. Air apparently leaked into toroid. Corrosion layer 0.00015 inch deep (0.15 in./year) on hot surfaces. Crystalline deposit on cooled sector 0.015 inch thick.
8	A nickel (99.4 Ni + Co)	Ni Cu Fe Mn Si C S	99 min 0.25 max .5 max .35 max .5 max .2 max .02 max	21	Insufficient for analysis	None			Ni Fe Cu Mn Cr Co NaOH	88.0 5.9 4.0 1.5 .3 .3	0.305 100.0	Nickel		1.10	Corrosion layer 0.00025 inch deep (0.10 in./year). Crystalline deposit on cooled sector 0.012 inch thick.

[1] All toroids were loaded with 108 grams of sodium hydroxide and a cover gas of helium prior to testing. Fluid velocity, 15 ft/sec; test temperature, 1500° F; temperature difference between hot and cooled sector, about 20° F.

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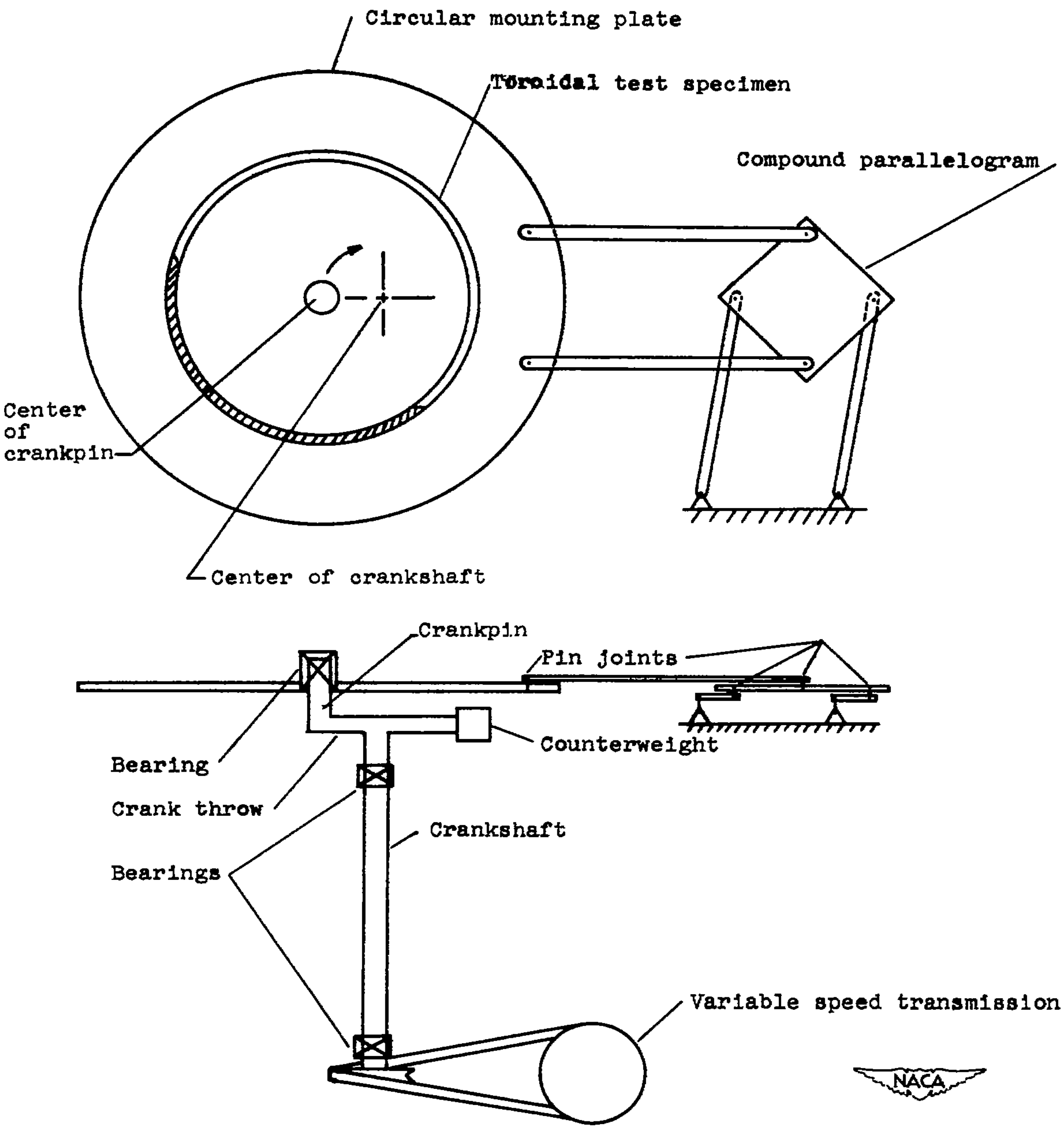

Figure 1. - Schematic diagram of circulating apparatus.

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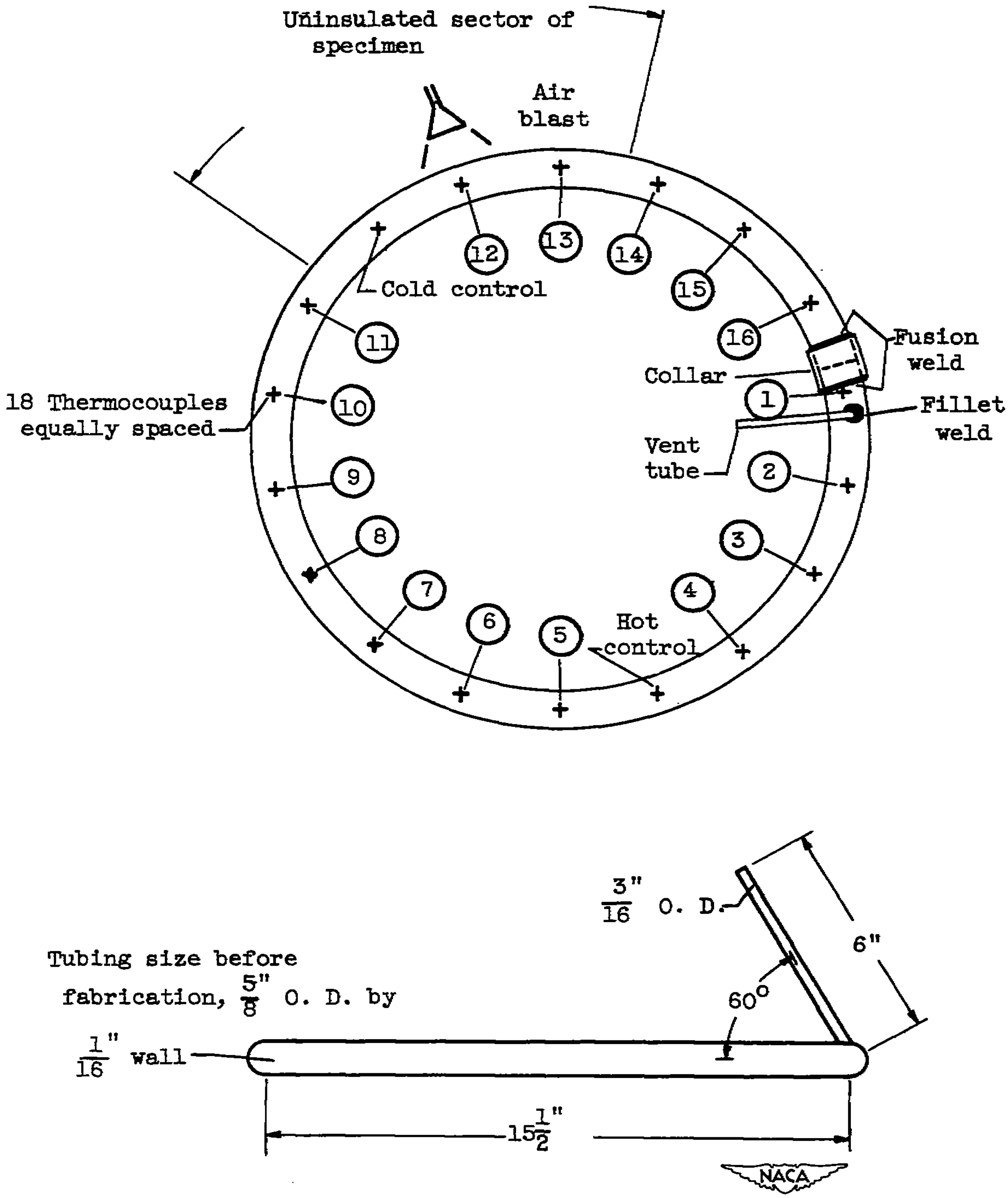

Figure 2. - Diagram of toroidal specimen.

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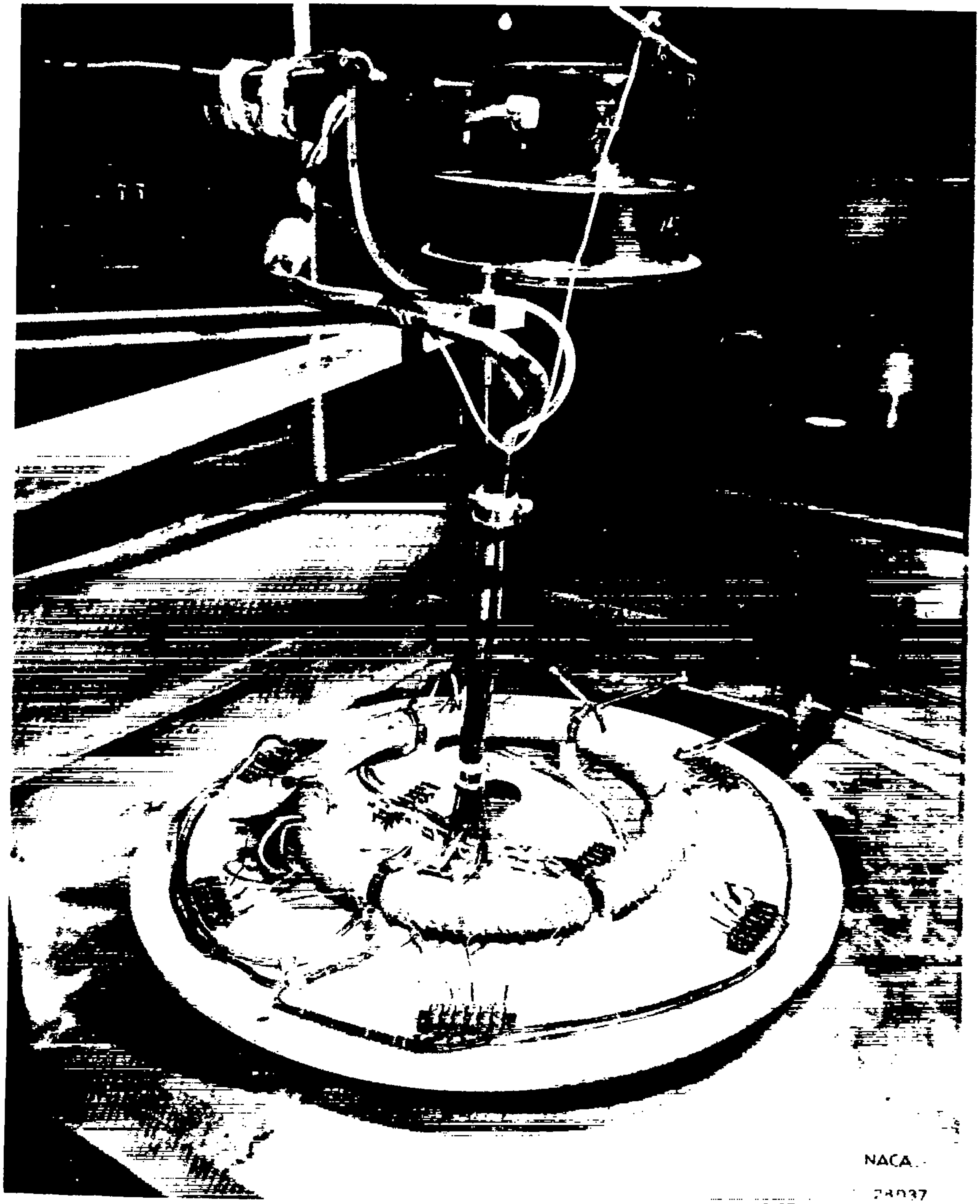


Figure 3. - Instrumented specimen installed in circulating apparatus.

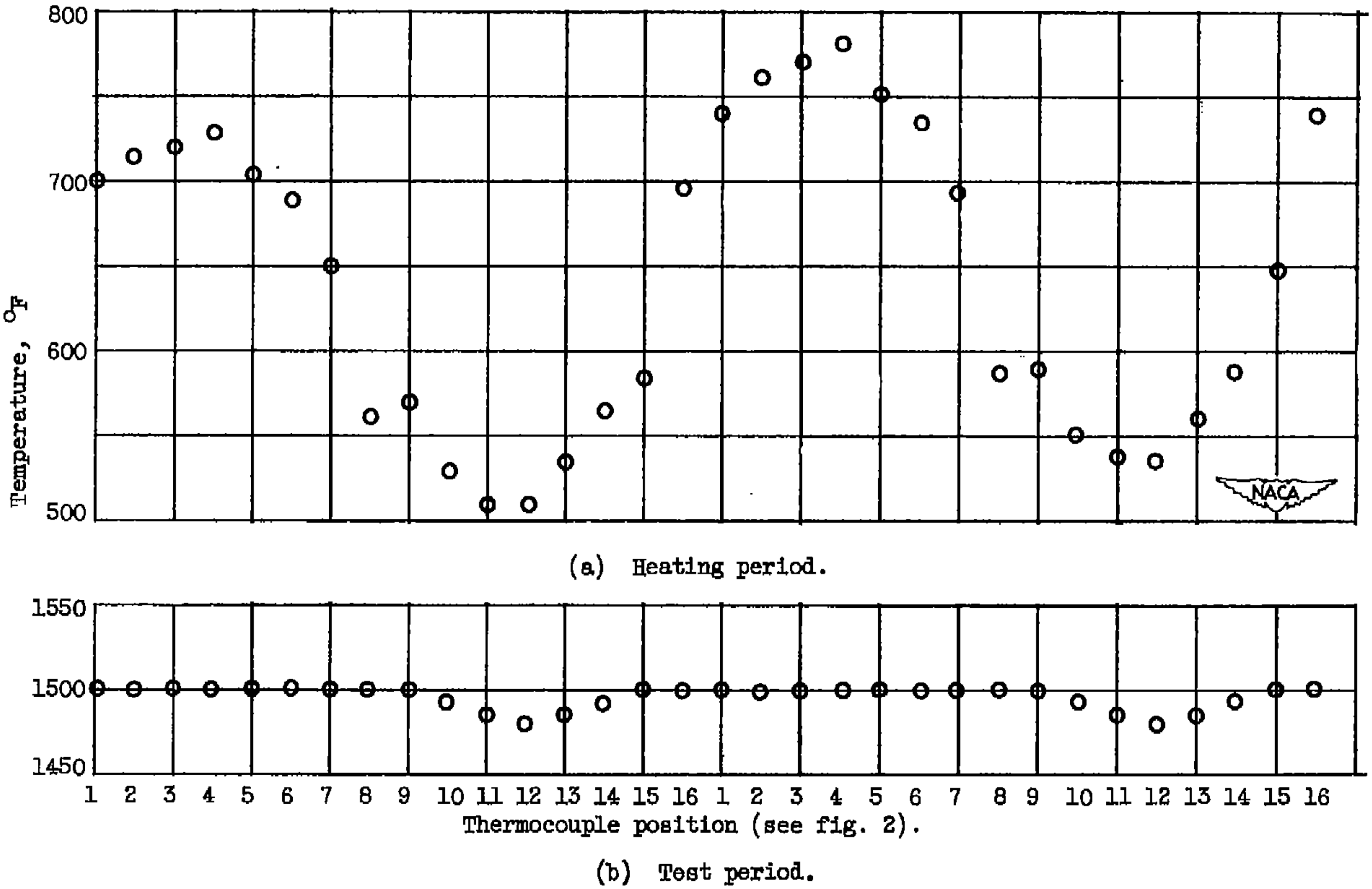
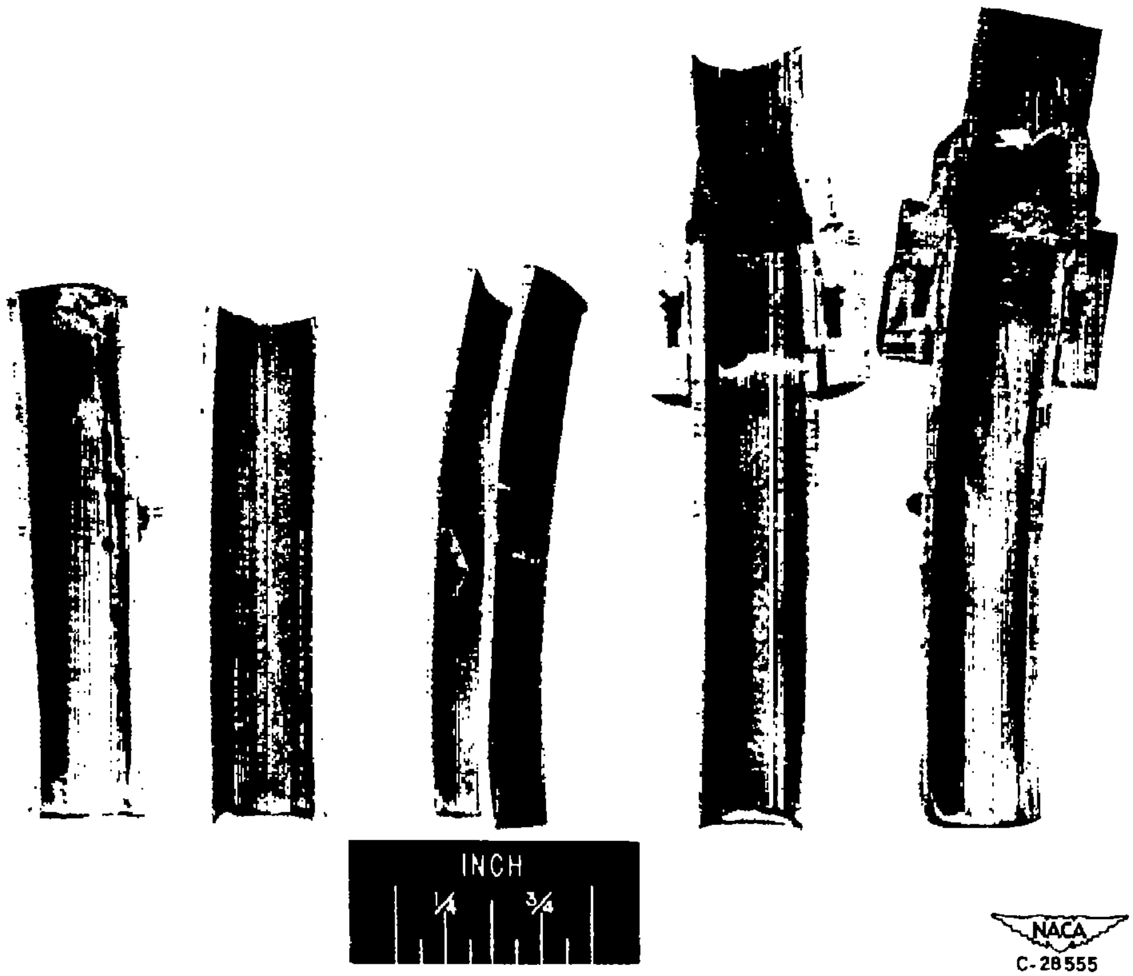
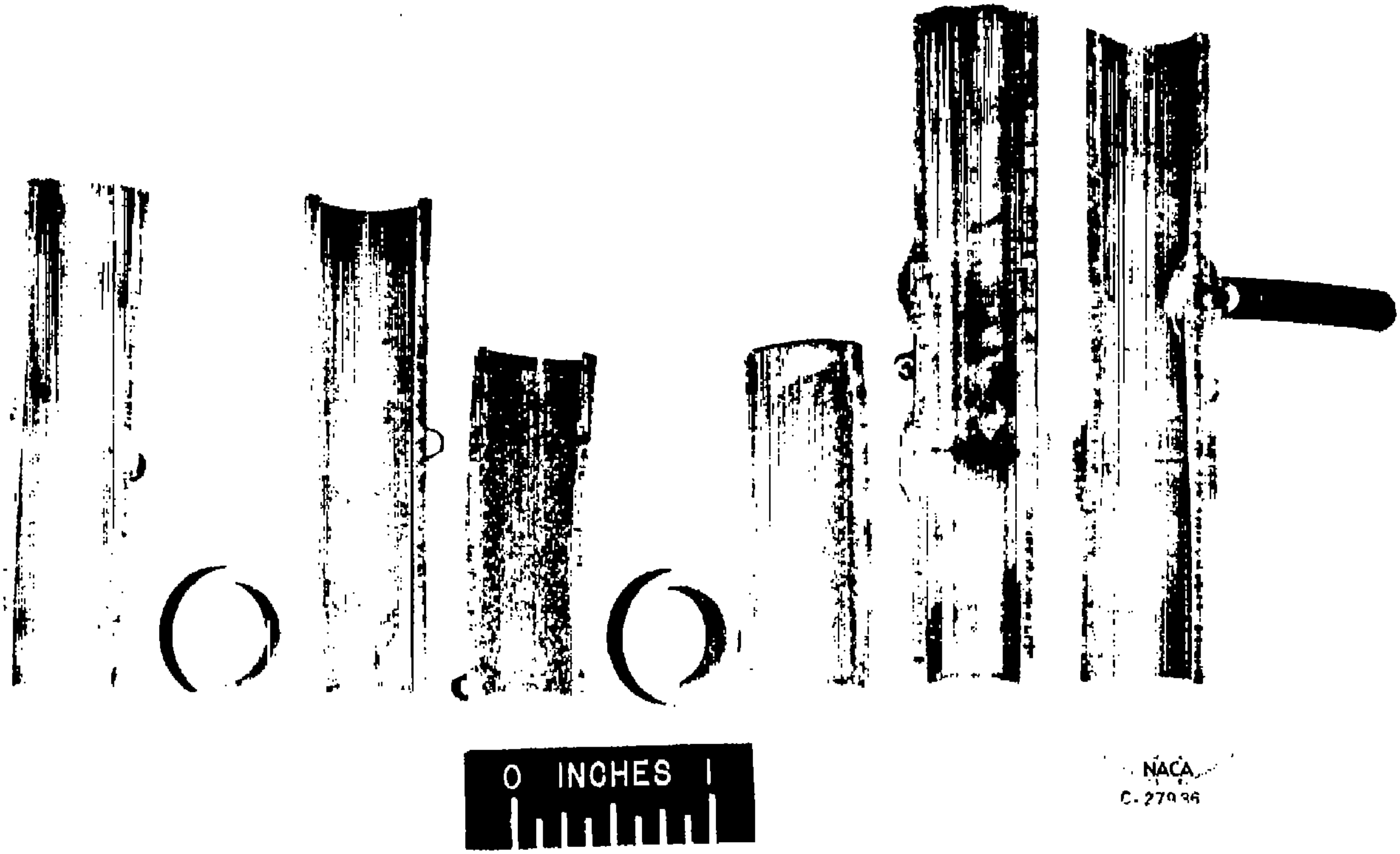


Figure 4. - Representative temperature distribution around toroid as measured by 16-point recording potentiometer.



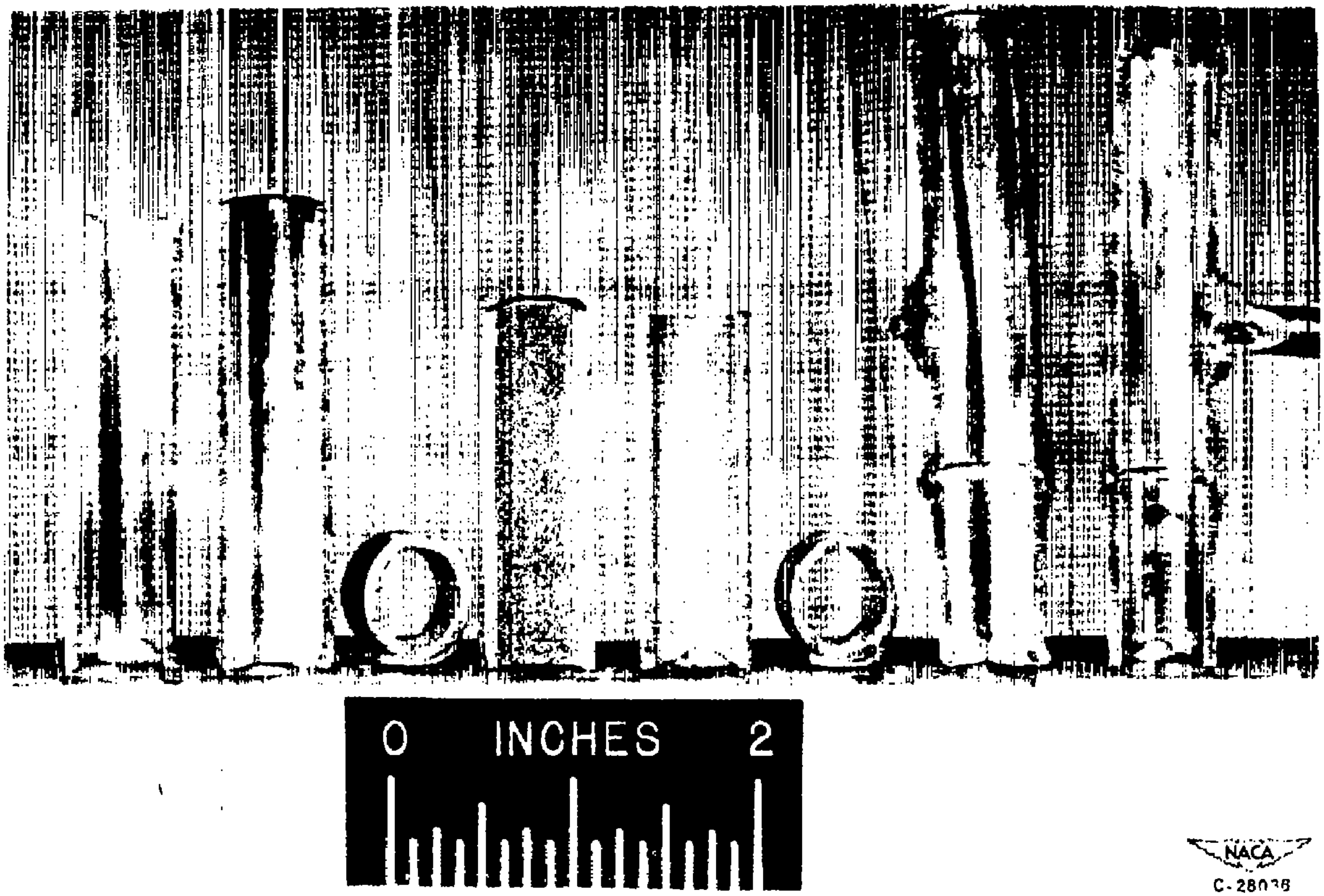
(a) Hot section. (b) Cooled section. (c) Closure.

Figure 5. - Condition of AISI 347 stainless steel (specimen 2) after 21 hours exposure to molten sodium hydroxide flowing at velocity of 15 feet per second, temperature of 1500° F, and circumferential temperature gradient of 20° F.



(a) Hot section. (b) Cooled section. (c) Welded closure.

Figure 6. - Condition of Inconel (specimen 4) after 24 hours exposure to molten sodium hydroxide flowing at velocity of 15 feet per second, temperature of 1500° F, and circumferential temperature gradient of 20° F.



(a) Hot section. (b) Cooled section. (c) Welded closure.

Figure 7. - Condition of type A nickel (specimen 7) after $8\frac{1}{2}$ hours exposure to molten sodium hydroxide flowing at velocity of 15 feet per second, temperature of 1500° F, and circumferential temperature gradient of 20° F.

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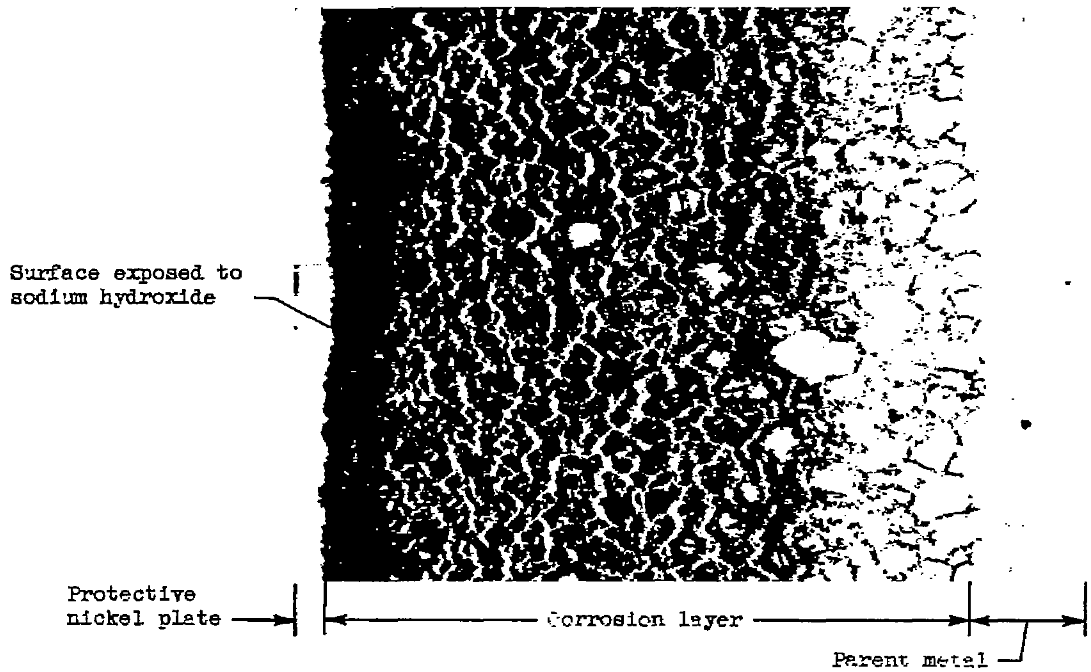
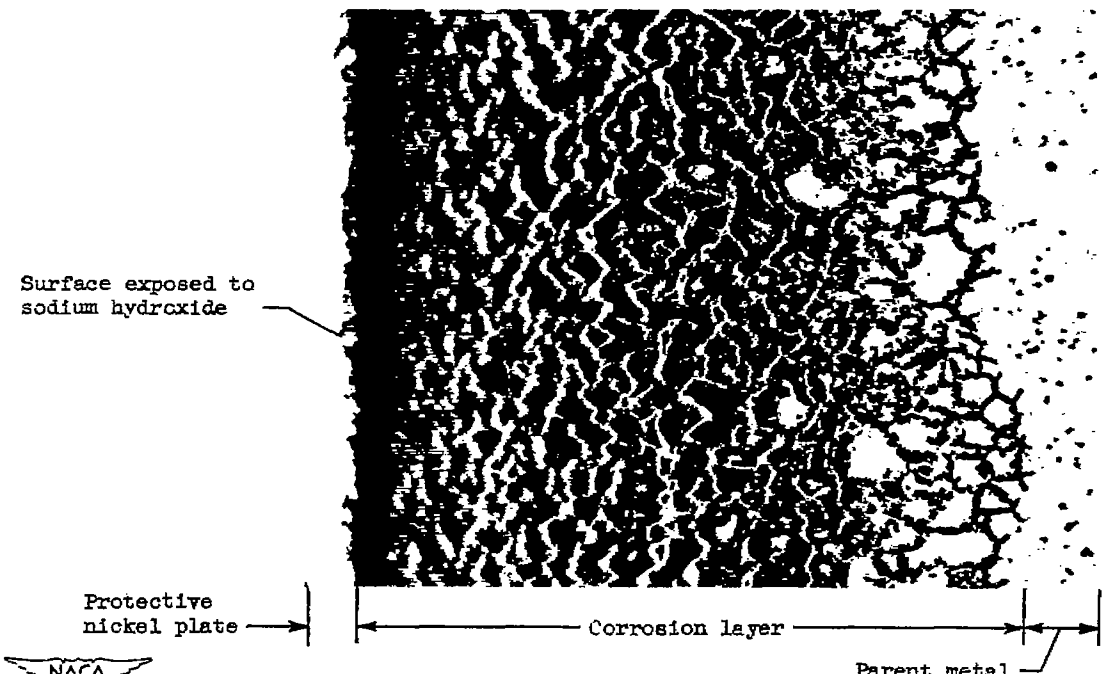


(a) Specimen from hot section.



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(b) Specimen from cooled section.

Figure 8. - Photomicrographs of AISI 347 stainless steel (specimen 2); X250; etchant, 10 percent oxalic acid electrolytic.

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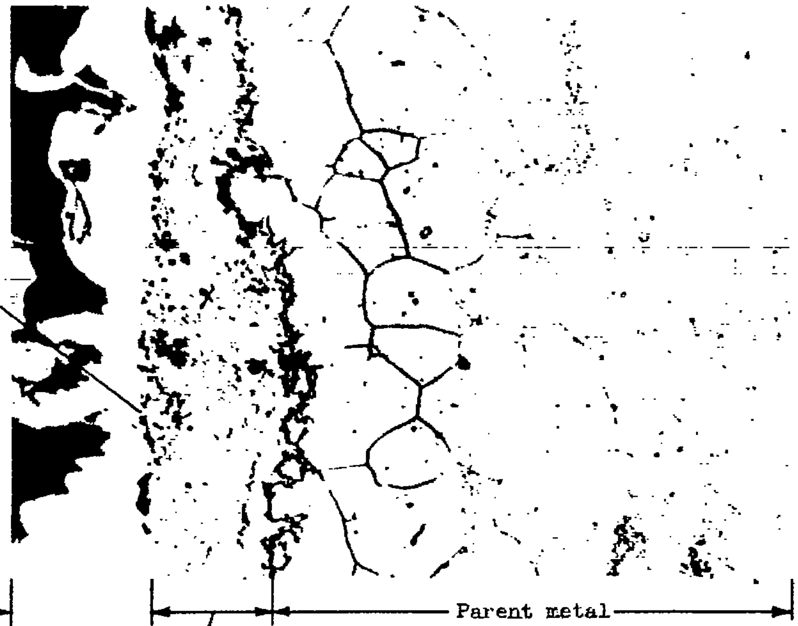
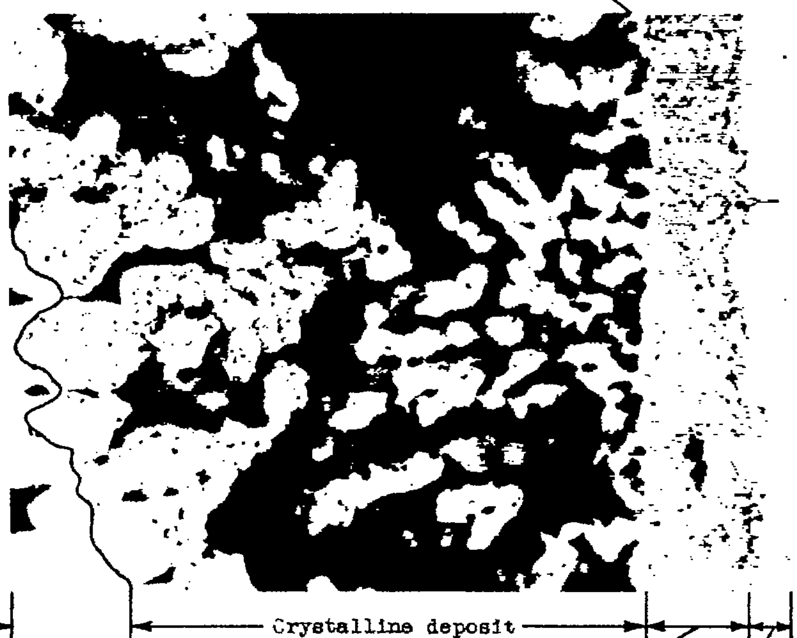


(a) Specimen from hot section.



(b) Specimen from cooled section.

Figure 9. - Photomicrographs of Inconel (specimen 4); X250; etchant, 5 percent oxalic acid electrolytic.

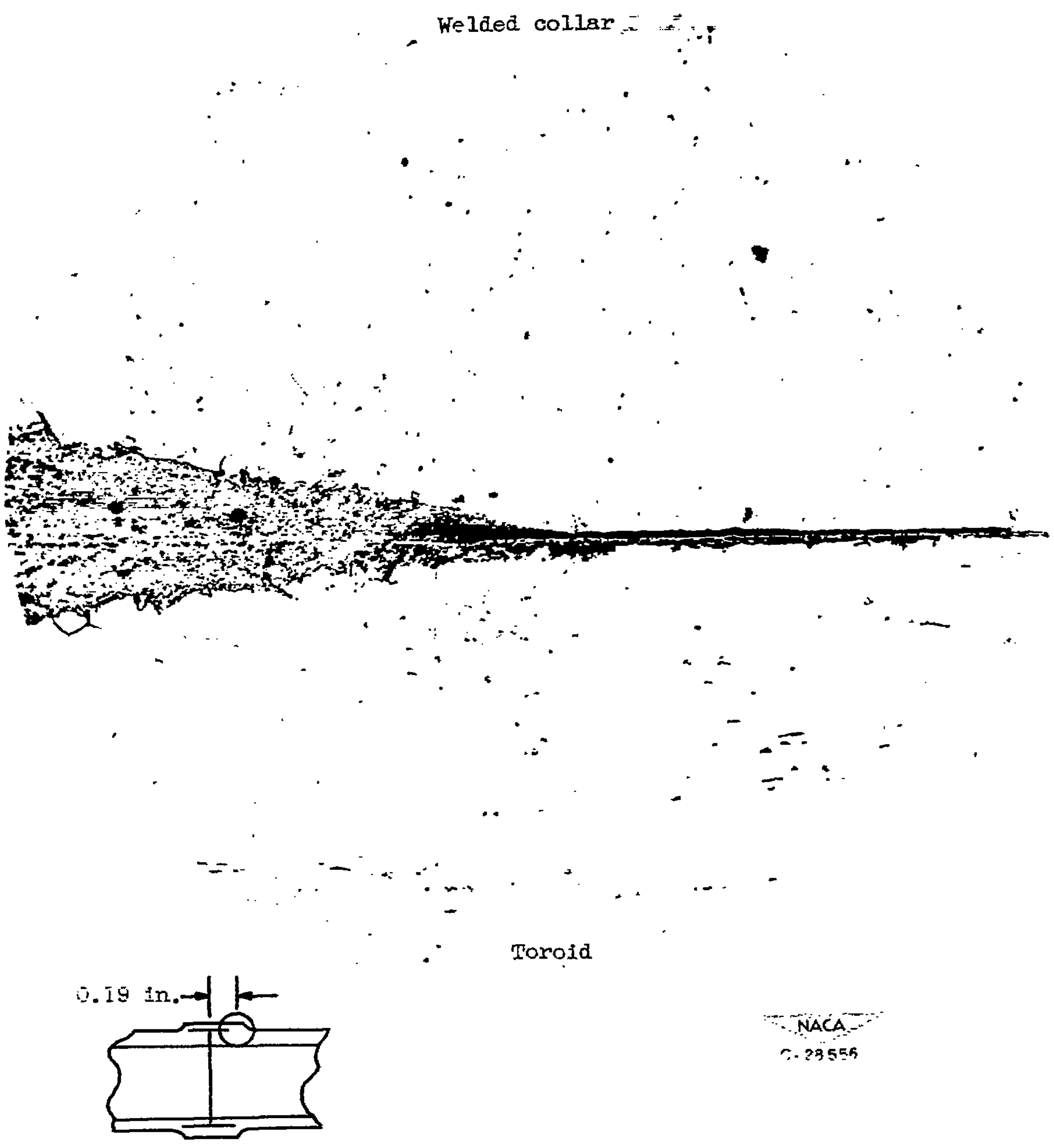
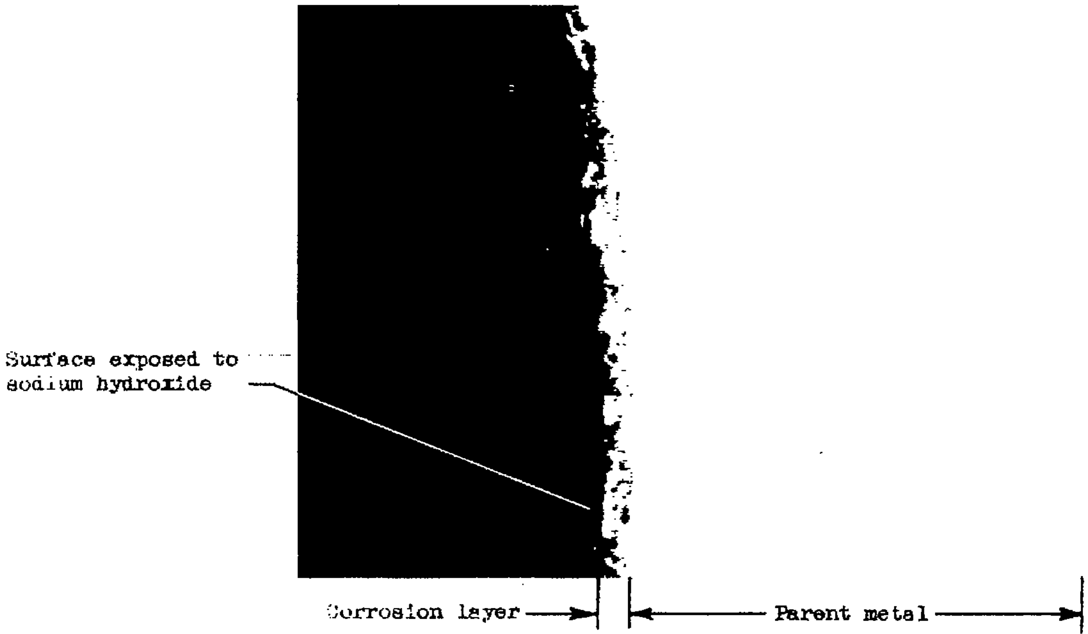
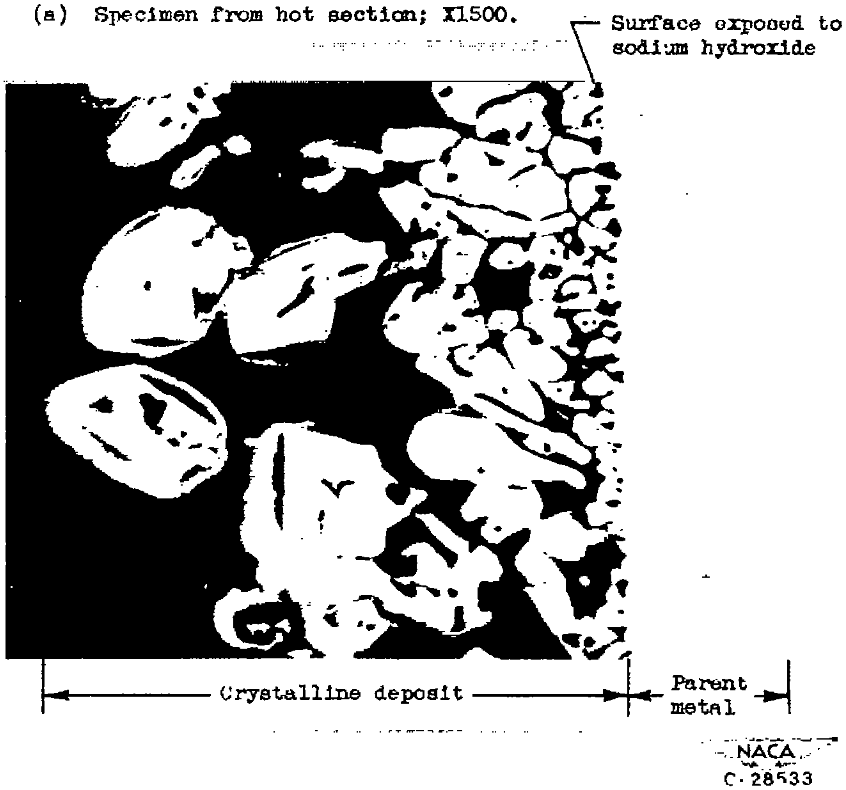


Figure 10. - Photomicrograph of section from welded closure of Inconel (specimen 4); X250; etchant, 5 percent oxalic acid electrolytic. Orientation of photomicrograph indicated by circle in sketch.

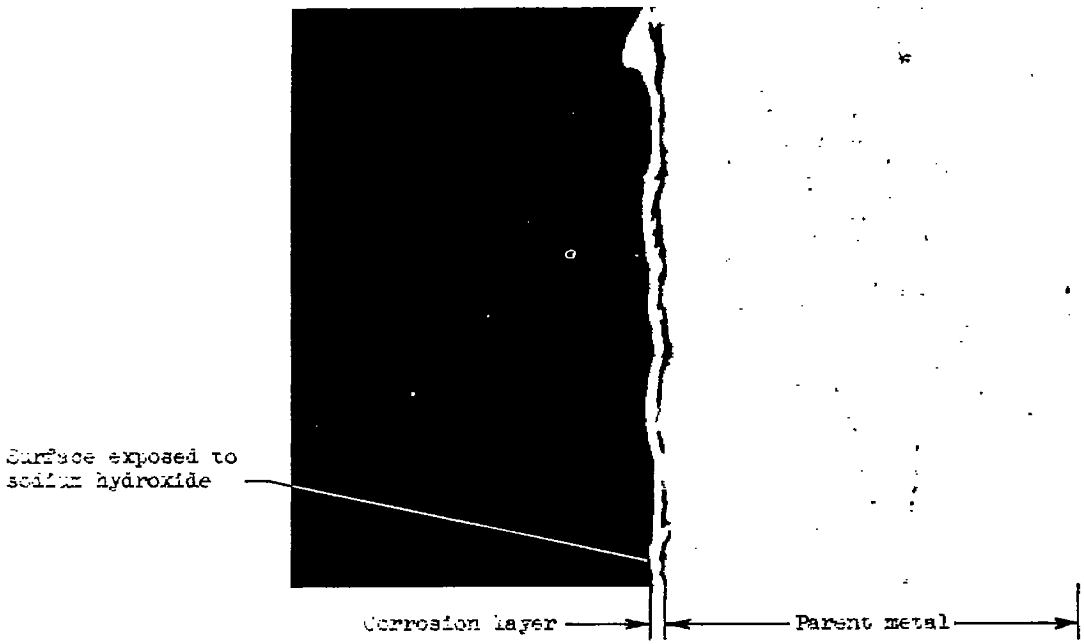


(a) Specimen from hot section; X1500.

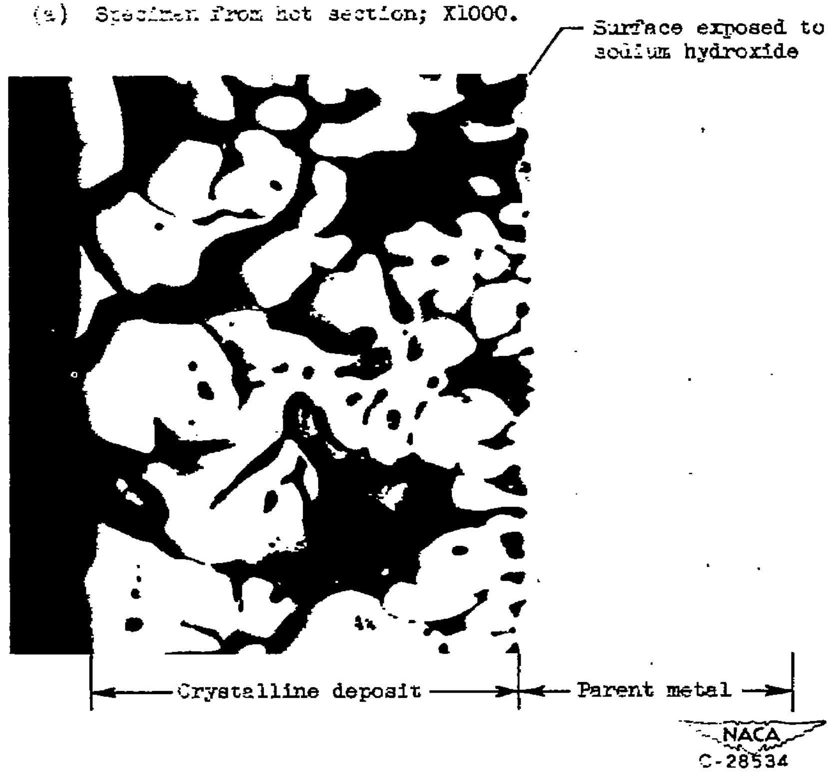


(b) Specimen from cooled section; X250.

Figure 11. - Photomicrographs of type A nickel (specimen 7); etchant, none.



(a) Specimen from hot section; X1000.



(b) Specimen from cooled section; X250.

Figure 12. - Photomicrographs of type A nickel (specimen 8); etchant, none.

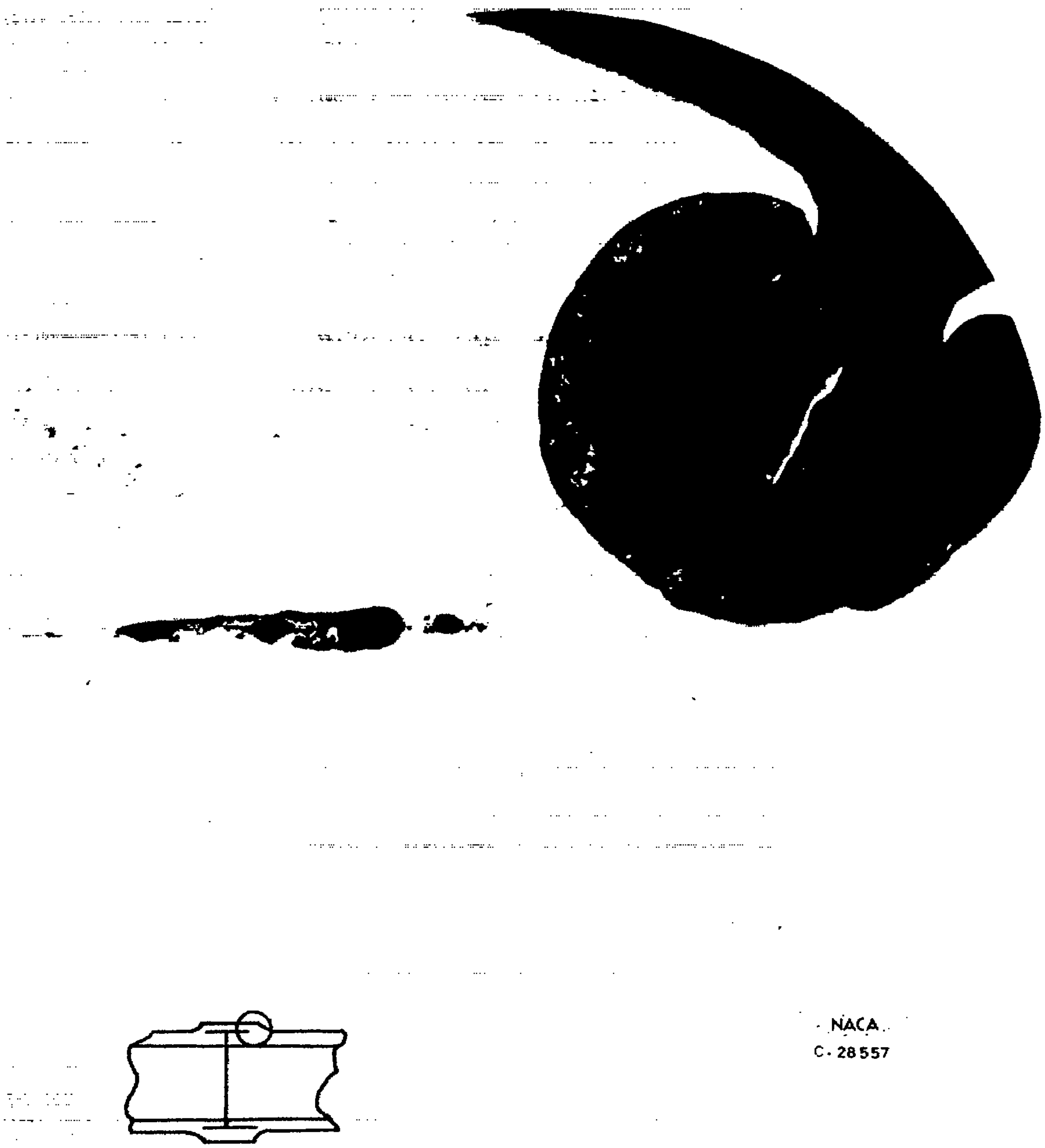


Figure 13. - Photomicrograph of welded section, type A nickel (specimen 7); X250; etchant, none. Orientation of photomicrograph indicated by circle in sketch.